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PROPERTIES OF PIEZOCERAMICS PRODUCED FROM LEAD ZIRCONATE-TITANATE POWDER OBTAINED BY PLASMA DENITRATION

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The effect of the sintering conditions on the properties of piezoceramic materials made of lead zirconate-titanate obtained by the plasma denitration method is demonstrated. The optimum sintering conditions for piezoceramic materials providing the maximum values of the electrophysical parameters are determined.

The method for synthesis of solid solutions of lead zirconate-titanate (LZT) used in industry is based on solid-phase reactions in the mechanical mixture of oxides (PbO, ZrO_2, TiO_2) and modifying additives [1]. The main disadvantage of the solid-phase technology is the complexity of the preparation of disperse powder with high sintering activity. Moreover, in this type of synthesis the production history of the initial material is of great significance, since it substantially affects the quality of the end product and often leads to deviations in the chemical composition of piezoceramics. The attempt to eliminate the effect of the initial components and to ensure dispersion and particle structure of the powder favorable for sintering motivated the intensive development of the chemical and combined methods for LTC synthesis.

One of these methods, the method for synthesizing piezoceramic materials from LTC powder obtained by plasma denitration, is now being developed at the Siberian Chemical Works [2].

In plasmachemical treatment of lead, zirconium, and titanium nitrate solutions and the modifying additive, the resulting powders have high dispersion (200 – 400 nm), significant specific surface density, high homogeneity, and complex phase compositions: the solid solution $Pb(Zr_{1-x}Ti_x)O_3$ (up to 60%; here and elsewhere mass content is indicated); lead, zirconium or titanium nitrate (up to 5%); lead oxide (up to 25%); titanium and zirconium dioxides (up to 8%). In comparison to the other methods the plasmachemical technology is distinguished for its high efficiency, low material consumption of the machinery used; and the possibility of continuous synthesis of LTC powder [2].

The present paper investigates the effect of the sintering conditions on the electrophysical parameters of piezoceramic products based on LTC powder obtained by the plasma denitration method.

LTC powder equivalent to the composition $Pb_{0.94} \cdot Sr_{0.06}(Zr0.53 \cdot Ti_{0.47})O_3$ was obtained in a plasma chemical plant (generator power 60 kW) from a mixture of initial nitrate solutions of lead, zirconium, and titanium and modifying additives [2]. Samples 25.5 mm in diameter were molded from LTC powder without adding any organic binder (molding pressure of 70 MPa). The apparent density of the molded samples was 4.0 – 4.5 g/cm^3.

According to traditional technology, the molded castings are put in hermetically sealed nickel packages filled with a lead-containing charge ($PbZrO_3$) and placed in a cold furnace of the chamber type. Heating begins from a temperature of 20 – 30°C at the rate of 300°C/h and reaches the working temperature (1200 – 1270°C), then it is held for 1 – 2 h, and after that the furnace is switched off. The samples are removed at a temperature of 20 – 100°C.

The initial plasma chemical LTC powder has a number of properties (high chemical activity, low sintering temperature, increased resistance to thermal loads; absence of organic binder in molding) that distinguish it from LTC powder synthesized by the solid-reaction method from a mechanical oxide mixture. These specific features of the initial plasmachemical powder make it possible to use the accelerated heating method in production of ceramics from this powder, which makes it possible to reduce significantly the duration of sintering of the articles (5 – 6 times shorter compared to the traditional technology) and power consumption, to increase the efficiency of the process, and to eliminate the lead-containing charge.

In order to establish the optimum synthesis procedure, the piezoceramic articles based on the LTC obtained by plasmachemical technology were sintered by the accelerated heating method in the temperature interval of 850 – 1250°C with a sintering duration of 15 – 120 min and a sample heat-

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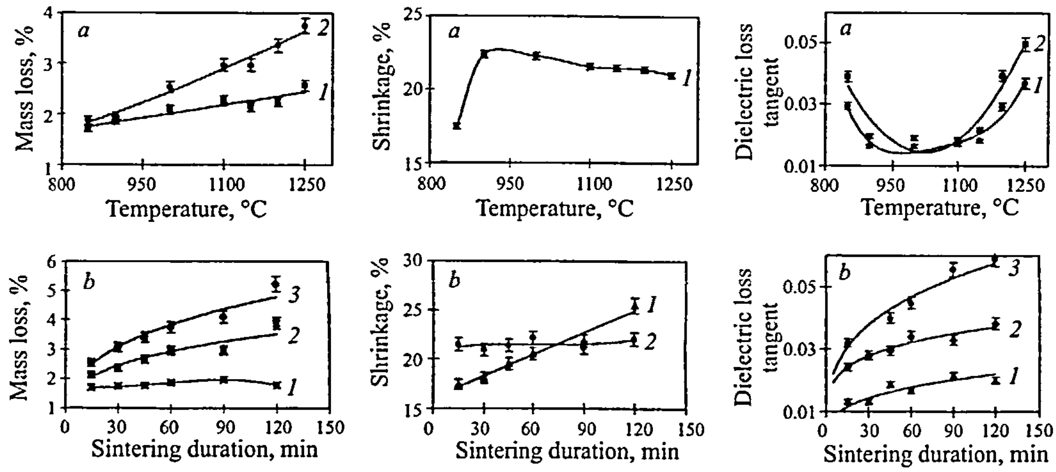

Fig. 1. Effect of the temperature (*a*) and sintering duration (*b*) on the mass loss of the piezoceramics sintered, linear shrinkage of the piezoceramics, and dielectric loss tangent. *a*) Sintering duration: *1*) 15 min; *2*) 60 min; *b*) sintering temperature: *1*) 850°C; *2*) 1150°C; *3*) 1250°C.

ing rate of 100 – 150°C/min. The molded samples were put inside the nickel packages without the lead-containing charge and sintered in a muffle furnace previously heated to the working temperature. Counting of the isothermal heating time started 5 min after placing the samples in the furnace. After the end of sintering, the piezoceramic samples were ground on a surface grinding machine, then their surface was degreased by boiling in a soap solution and calcined at the temperature of 250°C for 1 hour. The silver paste was deposited on the prepared surface and burned in at a temperature of 700°C. The samples with the electrodes applied were polarized in transformer oil at the temperature of 125°C for 30 min and the voltage of the polarizing field was 2.5 kW/mm. A pulse current source was used for polarization.

The dielectric and piezoelectric characteristics of the samples were measured according to OST 11 0444.

In sintering of piezoceramics (Fig. 1) based on LZT powder obtained by the plasma denitration method for 15 – 90 min at a temperature below 1150°C, the mass loss increases insignificantly, which is due to evaporation of moisture and decomposition of the nitrates contained in the sample. A more significant decrease in the sintered sample mass (up to 2.96%) starts at a temperature above 1100°C and sintering time over 60 min and is due to intense evaporation of lead oxide.

The linear shrinkage (Fig. 1) of the sintered piezoceramic articles at the temperature of 850°C grows with an increase in the duration of sintering and reaches the maximum values (25%) in sintering for 120 min. Up to the sintering temperature of 1000°C (sintering time of 15 min), the shrinkage tends to increase, and above that temperature with a duration of sintering over 30 min, the shrinkage varies within the limits of 20 – 22%. The pronounced linear increase in shrinkage with an increasing duration of sintering at low temperatures is determined by the unformed microstructure of the ceramics and stops only after lengthy heating at the temperature specified. The unformed structural state is confirmed by the low density values of the samples obtained at the temperature of 850°C sintered for 15 – 45 min (6.8 g/cm^3).

It was found that the conditions of sintering of piezoceramic products from LZT powder obtained by the plasma denitration method produce an effect on their parameters. The lowest values of the dielectric loss tangent are observed within the temperature interval of 1000 – 1100°C. As the temperature and sintering duration increase, the dielectric loss tangent grows significantly, which is caused by disturbance of the chemical composition of the samples sintered at the expense of intense evaporation of lead at temperatures above 1100°C (Fig. 1).

One of the main parameters of piezoceramic materials based on LZT is the relative resonance interval. This parameter is extremely sensitive to the conditions of sintering of piezoceramics based on LZT powder obtained by the plasma denitration method. The maximum values of the relative resonance interval were observed for samples sintered for 30 min at a temperature of 1100°C. (Fig. 2*a*). With a rise in the sintering temperature from 850 to 1100°C, the relative resonance interval increases. Within the temperature range specified, an increase in this parameter is observed also with a rise in the duration of sintering.

As the sintering temperature increases to 1200°C, the width of the relative resonance interval decreases sharply and with an increase in the sintering duration reaches its lowest values (Fig. 2*b*). Since the relative resonance interval is a structurally sensitive parameter and is determined to a great extent by the stoichiometric composition of the piezoceramic, it should be noted that the range of maximum values for this parameter is within the sintering temperature range of 1000 – 1100°C (sample heating rate of 100 – 150°C/min) with a duration of sintering of 15 – 45 min, i.e., these conditions can be considered the opti-

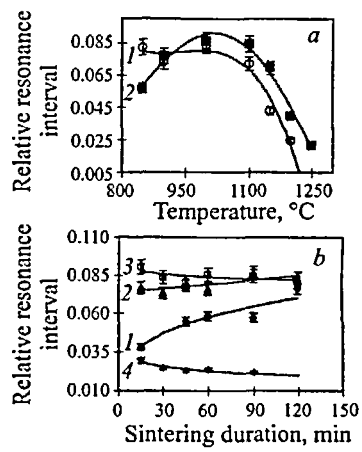

Fig. 2. Effect of the temperature (*a*) and sintering duration (*b*) on the value of the relative resonance interval of piezoceramics. *a*) Sintering duration: *1*) 30 min; *2*) 90 min; *b*) sintering temperature: *1*) 850°C; *2*) 1000°C; *3*) 1250°C.

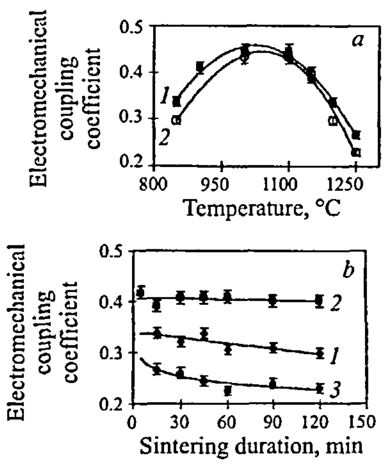

Fig. 3. Effect of the temperature (*a*) and sintering duration (*b*) on the electromechanical coupling coefficient of piezoceramics. *a*) Sintering duration: *1*) 15 min; *2*) 120 min; *b*) sintering temperature: *1*) 850°C; *2*) 1150°C; *3*) 1250°C.

mum ones for sintering of piezoceramics from LZT powder obtained by the plasma denitration method.

Figure 3 shows the dependence of the electromechanical coupling coefficient on the temperature and duration of sintering. The maximum values of this coefficient were found for samples sintered within the temperature range of 1000 – 1100°C (Fig. 3*a*). An increase in the sintering duration over the entire temperature range leads to a noticeable decrease in the electromechanical coupling coefficient. (Fig. 3*b*). It can be attributed to disturbance of the stoichiometric composition of the piezoceramic at the expense of lead evaporation from the samples sintered.

Thus, on the basis of the experiments performed, it can be stated that time-temperature synthesis procedures exert an obvious effect on the properties of piezoceramics from LZT powder obtained by the plasma denitration method. The maximum values of the dielectric and piezoelectric parameters are found within the temperature range of sintering of 1000 – 1100°C with a sintering duration of 15 – 45 min and satisfy the requirements imposed on piezoceramic products.

The high chemical activity of the initial plasmachemical LZT powder and its resistance to the temperature differences in sintering make it possible to use the accelerated heating method which shortens significantly the duration of the process, reduces energy consumption, and prevents evaporation of lead from the samples sintered.

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